Compressions of Si, MgO, and $ZrSiO_4$ to 8 GPa as measured with a WC-anvil x-ray apparatus and epoxy pressure medium

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The compressions of silicon, magnesium oxide, and zircon have been measured to 8 GPa with a tungsten-carbide opposed-anvil x-ray apparatus using a boron-epoxy gasket and epoxy as a pressure-transmitting medium. For silicon and magnesium oxide, the bulk modulus and its pressure derivative were obtained by fitting a second-degree polynominal to the x-ray data. For zircon, the bulk modulus was determined by fitting an equation of the form $(\Delta V/V_0) = -(P/B_0)$. The values of the bulk modulus and its pressure derivative are $B_0 = 99.4 \pm 8$ GPa, $B'_0 = 3.2 \pm 1$ for silicon; $B_0 = 166 \pm 10$ GPa, $B'_0 = 2.5 \pm 1$ for magnesium oxide; $B_0 = 222 \pm 20$ GPa for zircon. In all the cases, the present values of B_0 are in good agreement with those obtained from ultrasonic measurements. On the basis of these results it is suggested that the use of epoxy as a pressure-transmitting medium can greatly reduce the uniaxial stress component and improve the sample-pressure distribution in the study of materials possessing large shear strength.

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I. INTRODUCTION

The tungsten-carbide-anvil x-ray apparatus has been used extensively in the high-pressure study of solids.[1-4] A finely powdered sample is mixed with another material called the internal standard or pressure marker. The pressure on the internal standard is calculated from the observed volume change and the knowledge of the compressibility. It is then assumed that the pressure on the sample is same as the pressure on the internal standard. This method has been used successfully in the past in the determination of the equation of state of crystalline solids. During the course of such studies a number of cases[5-8] have been encountered wherein the bulk modulus determined by x-ray methods differs significantly from that determined ultrasonically. Sato *et al.*[7] suggested that such an anomaly arises from the stress anisotropy in the sample. From entirely different considerations it was shown by the present authors[9,10] and others[11,12] that the sample compressed between the opposed anvils can support appreciable uniaxial stress, which leads to the stress anisotropy in the sample. Though the study of the uniaxial stress component provides interesting information on the yield strength[10] of the materials, from the point of view of experimental measurement it is desirable to eliminate or minimize the uniaxial stress component. This can be done ideally by using a liquid pressure-transmitting medium. Halleck and Olinger[13] have suggested the use of beryllium gaskets to seal the fluid pressure-transmitting medium. We have used epoxy as a pressure-transmitting medium in conjunction with the conventional boron-epoxy gaskets, in the determination of the compressibilities of silicon, magnesium oxide, and zircon. The experimental details and the results are given in Secs. II and III, respectively.

II. EXPERIMENTAL DETAILS

The samples of silicon used in this study were 99.999% pure from Research Organic Inorganic, Ltd. The magnesium oxide was in the form of light powder from J.T. Baker Chemical Co. The zircon samples were recovered from pegmatite from Pacoima Canyon, San Gabriel Mountains, Calif. The zircon samples were light violet in color and produced sharp diffraction patterns. The lattice parameters were determined from the diffractometer records taken with CuK_α radiation. Using the diffraction lines in the range of $10° \leq \theta \leq 40°$, the lattice parameters were found to be $a = 6.607$ (± 0.003) and $c = 5.991$ (± 0.002). The density calculated from the unit cell dimensions and the number of formula units in the unit cell is 4.664 g cm^{-3}. No chemical analysis of the sample was made.

The experimental setup was the same as that used in the earlier investigations.[9,10] The samples were contained in a 0.2-mm hole at the center of a boron-epoxy disk 3.2 mm in diameter and 0.5 mm thick. The anvil faces were in the form of truncated cones with a 3.2-mm flat face and 85° half-cone angle.

The finely powdered sodium chloride was used as a pressure standard. The sample was not mixed with sodium chloride as is conventionally done. Instead, a calibration run was made with sodium chloride alone in the sample position. The powdered sodium chloride was mixed with Scotch "Household" epoxy in the volume ratio 1:5. The slurry was carefully placed in the central hole of the boron-epoxy disk, and 24 h were allowed for the epoxy to set. The flat faces of the boron-epoxy disk were carefully lapped in a jig to a thickness of 0.3 mm. The boron-epoxy disk, with the NaCl-epoxy mixture in the sample position, was pressed between the anvils to a nominal pressure of 1 GPa. The pressure was released to 1 atm. The disk was then compressed to various pressures and the diffraction pattern was taken at each pressure. A calibration curve between the hydraulic pressure of the ram and the pressure generated on NaCl was drawn. After the calibration

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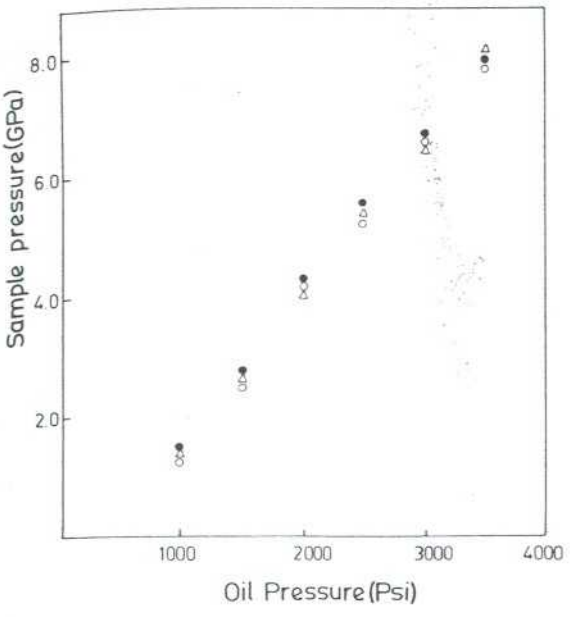

FIG. 1. A sample-pressure—vs—ram-oil-pressure curve. Three different symbols show data from three separate runs.

curve was determined, the boron-epoxy disks from the same batch were used in experiments with the samples. The finely powdered sample was mixed with epoxy in the volume ratio 1 : 5, and finished to the same final dimensions as in the case of the calibration run. After the initial compression treatment similar to that in the calibration run, the volume compressions of the sample were measured at various hydraulic pressures of the ram. The ram hydraulic pressures were converted to pressure on the sample using the calibration curve.

III. RESULTS AND DISCUSSION

A. Pressure calibration

Before discussing the results, a few comments on the use of the epoxy as a pressure-transmitting medium and on the calibration procedure is in order. The idea of using epoxy as a pressure-transmitting medium is not new. In the past, epoxy has been used as a pressure-transmitting medium in opposed-anvil apparatus.[14] The piezoresistivity measurements[14] have shown that the pressure is hydrostatic within 0.1 GPa above 3 GPa. We have studied the performance of the epoxy as the pressure-transmitting medium in a Bridgman anvil setup by measuring the resistance of Bi as a function of pressure and comparing it with the results obtained with a AgCl pressure transmitter. With epoxy, Bi I—Bi II and Bi II—Bi III transitions are sharp and very well resolved. The Bi III—Bi V transition is also sharp.[15]

The sample is completely surrounded by epoxy; therefore the uniaxial stress component is of the order of the uniaxial stress that epoxy can support. The uniaxial stress component sustained by epoxy can be estimated, if the yield strength of epoxy at 1 atm and its pressure derivative are known. The yield strength of epoxy was measured under static load and was found to be 0.036 GPa.[16] It has been shown[17,18] that the pressure derivative of the yield point is approximately equal to (B_0'/B_0), where B_0 and B_0' are the bulk modulus and the pressure derivative of the bulk modulus, respectively. The parameters B_0 and B_0' were estimated from the pressure-volume relation determined in a piston-cylinder apparatus. A value of 1.2 GPa^{-1} was obtained for (B_0'/B_0). Assuming a linear relation between the yield strength and pressure, these data give a value of nearly 0.5 GPa for the yield strength at 10 GPa. However, in analogy with the variation with pressure of many other properties, such as elastic constants, the yield strength is not expected to vary linearly over a wide range of pressure. One would expect, in general, a negative nonlinear term. Thus the uniaxial stress component is likely to be less than 0.5 GPa.

The validity of the calibration procedure depends on the high degree of reproducibility of the ram-oil-pressure versus sample-pressure relation in various runs. The calibration curve may show systematic variations because of the variations in the ratio of boron and epoxy in the boron-epoxy disk and in the dimensions of the boron-epoxy disks. To estimate the reproducibility of the calibration curve, separate runs were made disks. The results are shown in Fig. 1. The uncertainty in pressure determination was nearly ±0.15 GPa. When the disks prepared from the different batches of boron-epoxy mixtures were tested, the calibration curves were found to differ slightly. This was thought to be due to slight variations in the ratio of boron and epoxy. The disks from each batch were calibrated separately. The calibration curves showed considerable variations if the epoxy in the boron-epoxy disk was not allowed to set completely. For this reason, the boron-epoxy disks were shelved at room temperature for at least four weeks before use.

It might be argued that the calibration curve determined with sodium chloride may not be valid for the sample with elastic properties very different from those of sodium chloride, because of the different degree of pressure intensification[19] with different samples. However, during the determination of the compressibilities of MgO, CaO, and NaF, Sato *et al.*[7] found that the intensification factors for all these materials

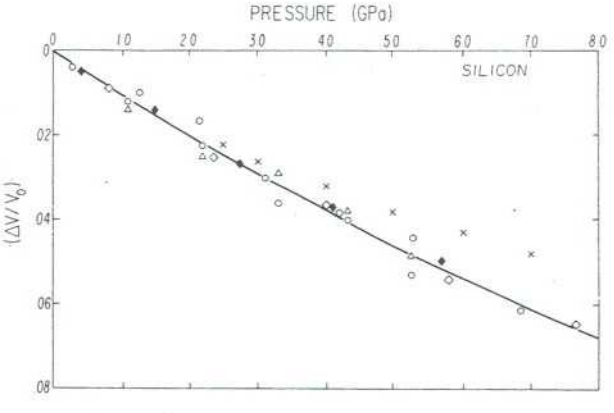

FIG. 2. $(\Delta V/V_0)$-vs-pressure plot for silicon. Bridgman's data (Ref. 22) are shown by crosses. Other symbols indicate different runs from the present experiment.

TABLE I. B_0 and B_0' for silicon. PC—piston cylinder; ME—Murnaghan equation; PE—polynomial equation.

No.	B_0 (GPa)	B_0'	Method	Reference
1	97.80	4.17	Ultrasonic[a]	20
2	98.40	4.66	PC—ME	21
	98.80	3.94	PC—PE	
3	92.05	15.3	PC—ME	22
4	100.08	4.72	PC—ME	23
	97.93	4.68	PC—PE	
5	82.0	1.7	x-ray, cubic press	24
6	99.4 ± 8	3.2 ± 1.0	x-ray PE	Present study
	92.0 ± 7	6.0 ± 2.0	ME	

[a] The ultrasonic values were converted to isothermal as suggested in Refs. 25 and 26.

TABLE II. B_0 and B_0' for magnesium oxide. PE—polynomial equation; ME—Murnaghan equation.

No.	B_0 (GPa)	B_0'	Method	Reference
1	160.0	4.16	Ultrasonic[a]	27
2	159.6	4.44	Ultrasonic[a]	28
3	159.6	4.29	Ultrasonic[a]	29
4	160.5	3.89	Ultrasonic[a]	30
5	166.0 ± 10	2.5 ± 1	x ray, PE	Present study
	168.3 ± 10	2.5 ± 1	ME	

[a] The ultrasonic values were converted to isothermal as suggested in Refs. 25 and 26.

and for NaCl were the same, and it was possible to use a calibration curve to determine the sample pressure. Our unpublished results on Si, MgO, and NaCl also suggest that the intensification factor is independent of the sample used. In the present experiments the situation is much improved by diluting the sample with large amounts of epoxy. The elastic properties of the sample-epoxy mixtures do not differ as much as these do for the undiluted samples. This situation is more favorable to a sample-independent intensification factor.

B. Compressibility of Si

The $(\Delta V/V_0)$-vs-pressure data are shown in Fig. 2. The bulk modulus B_0 and its first derivative B_0' were obtained by fitting to the $(\Delta V/V_0)$-P data a second-degree polynomial in P. The values are $B_0 = 99.4 \pm 8$ GPa and $B_0' = 3.2 \pm 1.0$. The results of fitting a Murnaghan's equation are $B_0 = 92.0 \pm 7$ GPa and $B_0' = 6.0 \pm 2$. A comparison between the present results and the results of the other investigators is shown in Table I. It is seen that the present value of B_0 is in excellent agreement with the results of ultrasonic experiments by McSkimin and Andreatch,[20] and also with those of Bridgman[21,22] and Vaidya and Kennedy,[23] obtained by piston-cylinder apparatus. The present value of B_0' seems to be slightly smaller than the value obtained in ultrasonic experiments or in piston-cylinder measurements, but the differences seem to be within the errors in the determination of B_0'.

Recently, Seno *et al.*[24] reported measurements on Si in a cubic press. The values of both B_0 and B_0' are significantly smaller than the present values or the values reported by the earlier investigators.

The $(\Delta V/V_0)$-vs-P data to 10 GPa reported by Bridgman[22] are systematically smaller than the present values or the values estimated from the ultrasonic data (Fig. 2). The difference between the present value of $\Delta V/V_0$ and Bridgman's value at 8 GPa, for example, is nearly 30%.

C. Compressibility of MgO

The $(\Delta V/V_0)$-vs-P data are plotted in Fig. 3. The values of B_0 and B_0' were 166 ± 10 GPa and 2.5 ± 1, respectively, as obtained by fitting a second-degree polynomial. When the data were fitted to Murnaghan's equation of state, the corresponding values were $B_0 = 168 \pm 10$ and $B_0' = 2.5 + 1$. A comparison of the present values of B_0 and B_0' with those obtained by other investigators is given in Table II. It is seen that the present value of B_0 is in good agreement with the values obtained in ultrasonic experiments by Bogardus,[27] Anderson and Andreatch,[28] Chang and Barsch,[29] and

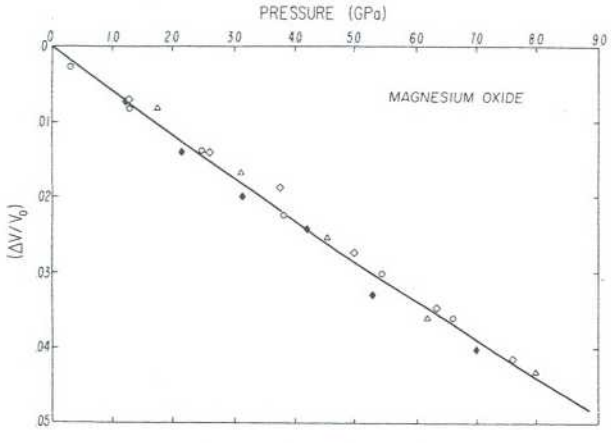

FIG. 3. $(\Delta V/V_0)$-vs-pressure plot for magnesium oxide. Independent runs are shown by different symbols.

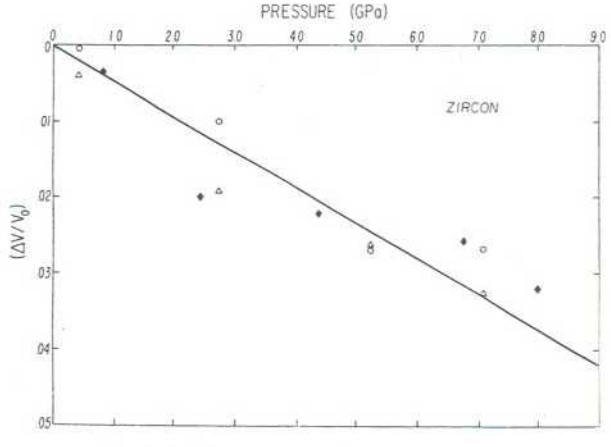

FIG. 4. $(\Delta V/V_0)$-vs-pressure plot for zircon. Independent runs are shown by different symbols.

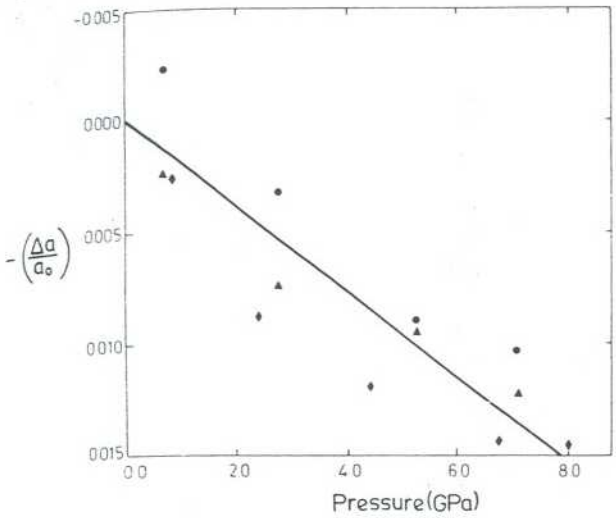

FIG. 5. $(\Delta a/a_0)$-vs-pressure plot for zircon.

Spetzler.[30] However, the value of B_0' is smaller than those obtained in other experiments.

The measurements on the 1:1 (by volume) mixtures of NaCl and MgO were also made to check the results reported by Sato *et al.*[7] Fitting a second-degree polynomial to 15 data points in the range $0.8 \leq P \leq 6.0$ gave $B_0 = 216 \pm 10$ GPa and $B_0' = -2.2 \pm 1$. The values obtained by Sato *et al.*[7] were $B_0 = 210 \pm 8$ GPa and $B_0' = -3.1 \pm 1.3$. Thus our results support the observations of Sato *et al.*[7] It is interesting to note that the use of epoxy as a pressure-transmitting medium yields a value of B_0 which is in good agreement with those obtained from ultrasonic experiments. The value of B_0' obtained with the use of epoxy as a pressure transmitter is positive and not negative as in the case when the conventional method of mixing sodium chloride and magnesium oxide is used.

D. Compressibility of zircon

The a-, c-, and $\Delta V/V_0$-vs-pressure data are plotted in Figs. 4–6. Since the bulk modulus of zircon is large as compared to the highest pressure reached in these experiments, only B_0 was determined by fitting the data to a linear relation between $\Delta V/V_0$ and P. A value of 222 ± 20 GPa was obtained for B_0. This value together with those obtained by other investigators are listed in Table III. The values of $(\partial a/\partial P)/a_0$ and $(\partial c/\partial P)/c_0$ were also obtained by assuming a linear relation between the lattice parameters and the pressure. The present results together with those of other investigators are listed in Table IV.

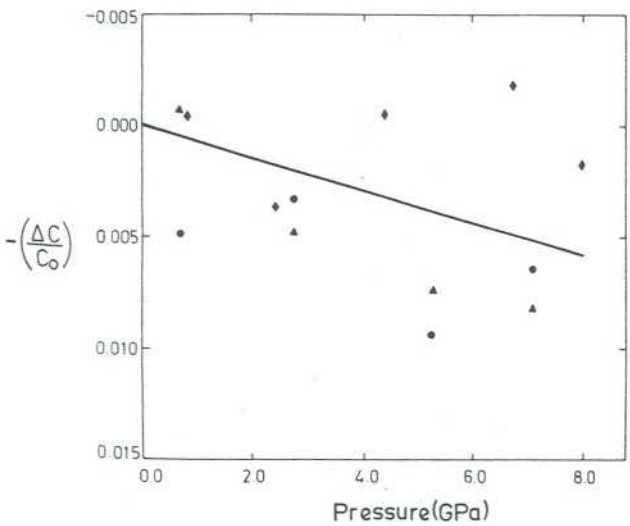

FIG. 6. $(\Delta c/c_0)$-vs-pressure plot for zircon.

TABLE III. B_0 and B_0' for zircon.

No.	B_0 (GPa)	B_0'	Method	Reference
1	220.2	• • •	Ultrasonic	8
2	200.0	• • •	Ultrasonic	31
3	373.0	• • •	x ray	32
4	388.0	• • •	Neutron	32
5	380.0	• • •	x ray	8
6	216	• • •	Polycryst. sample	33
7	222 ± 20	• • •	x ray	Present study

The naturally occurring mineral zircon contains radioactive impurities uranium and thorium, which emit α particles. The particles cause radiation damage to the crystals. The physical properties of zircon differ from one sample to another because of the different degree of radiation damage.[34–36] It is therefore important to consider this factor while comparing the results of various investigations.

The present samples produced sharp diffraction peaks which did not show any broadening or skewing.[34] As described in Sec. II, the lattice parameters were found to be $a = 6.607$ (± 0.003) and $c = 5.991$ (± 0.002) for the samples used in the present study. These values compare very well with the values reported for nonmetamict and synthetic zircon (for a comparison see Table V). Holland and Gottfried[34] have shown, for Ceylon zircon, that the lattice parameters depend on the α activity of the sample; the higher the α activity the larger are the lattice parameters. If a similar α activity–vs–lattice-parameter relation is assumed for the present sample, then it turns out that the present samples have very low α activity and are nearly nonmetamict.

Of the three independent ultrasonic measurements available in the literature, the one by Bhimasenachar

TABLE IV. $(\partial a/\partial P)/a_0$ and $(\partial c/\partial P)/c_0$ for zircon.

No.	$-(\partial a/\partial p)/a_0$ [$\times 10^3$ (GPa)$^{-1}$]	$-(\partial c/\partial p)/c_0$ [$\times 10^3$ (GPa)$^{-1}$]	Method	Reference
1	0.92 ± 0.07	0.83 ± 0.21	x ray	32
2	1.03 ± 0.07	0.57 ± 0.03	Neutron	32
3	0.96[a]	0.77[a]	x ray	8
4	1.725	0.989	Ultrasonic	8
5	1.91 (0.13)[b]	0.72 (0.21)[b]	x ray	Present study

[a] The values have been read from Fig. 1 of Ref. 8.
[b] Standard deviation.

TABLE V. Lattice parameters and densities of zircons used in various investigations.

No.	a_0 (Å)	c_0 (Å)	Density (g/cm^3)	Remarks	Reference
1	6.602	5.980	4.70	Natural, Nonmetamict	34
2	6.604	5.979	4.668		37
3	6.607	5.982	4.714		38
4	• • •	• • •	4.70	Natural	31
5	6.606 ± 0.001	5.980 ± 0.001	4.649	Synthetic	8
6	6.606 ± 0.001	5.980 ± 0.002	4.675	Natural Nonmetamict	8
7	6.607 ± 0.003	5.991 ± 0.002	• • •	Natural	Present study

and Venkataratnam[39] appears to be in gross error. The results of the other two investigations[8,31] also differ significantly. Özkan *et al.*[8] have shown that the elastic constants of metamict zircon are smaller than those for nonmetamict zircon samples. On the basis of this, it seems likely that the value of B_0 reported by Ryzhova *et al.*[31] are smaller than that reported by Özkan *et al.*[8] because the samples were damaged in the case of former.

The present measurements yield a value of 222 ± 20 GPa for B_0. This agrees very well with the value of 220.2 GPa obtained by Özkan *et al.*[8] The present value does not agree with the results of other x-ray-diffraction,[8,32] and neutron-diffraction studies.[32] Worlton *et al.*[32] reported a value of 373 GPa from x-ray-diffraction studies and 338 GPa from neutron-diffraction studies. Özkan *et al.*[8] obtained a value of 380 GPa for B_0 from x-ray-diffraction studies.

The values of $(\partial a/\partial P)/a_0$ and $(\partial c/\partial P)/c_0$ obtained by various investigators are listed in Table IV. The present value of $(\partial c/\partial P)/c_0$ is in reasonably good agreement with those obtained by Özkan *et al.*[8] and by Worlton *et al.*[32] in x-ray-diffraction experiments. The agreement of the present value of $(\partial c/\partial P)/c_0$ with the ultrasonic value is reasonably good. The present value of $(\partial a/\partial P)/a_0$ differs from the results of earlier measurements[8,32] by a factor of nearly 2, but agrees well with the ultrasonic value.[8] The data points show larger scatter in the $(\Delta c/c_0)$-vs P plot (Fig. 6) than that in the $(\Delta a/a_0)$-vs-P plot (Fig. 5). This is reflected in a larger standard deviation of $(\partial c/\partial P)/c_0$. Also, from the analysis of the x-ray data we find that the standard deviation of c is more than that of a. As was pointed out by Worlton *et al.*,[32] the larger standard deviation in c arises because the observed diffraction lines do not have large l values.

Ryshkewitch[33] determined the Young's modulus and the rigidity modulus of sintered zircon compacts. Assuming an isotropic behavior of these compacts, and using the well-known relation among the Young's modulus, the rigidity modulus, and the bulk modulus, a value of 216 GPa was obtained for the bulk modulus. This value is in good agreement with the present value.

IV. CONCLUSIONS AND SOME FURTHER REMARKS

The discrepancies observed between the values of B_0 obtained from earlier x-ray experiments and the ultrasonic experiments in case of magnesium oxide and zircon are not observed in the present study. The values of B_0 derived from the present x-ray-diffraction data are in good agreement with those obtained from ultrasonic measurements in all the three materials studied. It is generally noted that the value of B_0', obtained by fitting to the x-ray data a polynominal or Murnaghan's equation, is very small and sometimes even negative. The present values of B_0' are in better agreement with the values obtained ultrasonically. The set of B_0 and B_0' values obtained by fitting a polynomial equation differs slightly from the set of values obtained by fitting Murnaghan's equation. However, in view of relatively large errors inherent in x-ray measurements, these differences are not significant.

The errors of measurements in the present experiments, as derived from the scatter in x-ray data, are not much smaller than those in the experiments of other investigators. It appears that the use of epoxy as a pressure-transmitting medium reduces the magnitude of the uniaxial stress component and the systematic errors arising from it. Thus the improvements in the present results are because of an improved hydrostaticity of the pressure.

It might appear advantageous to mix the epoxy with a mixture of the sample and the standard, and thereby obviate the necessity of a separate calibration run. The diffraction lines from the sample and the standard are much stronger when these are mixed separately with epoxy than when the same proportion of epoxy is mixed with a sample-standard mixture. Further, the use of a sample-standard mixture has always had a disadvantage that some of the diffraction lines from the two materials fall close or overlap. In either case, a precise reading of the film is difficult. When the sample and the standard are used separately, good diffraction patterns are obtained even after these are diluted with large amounts of epoxy. In the case of sodium chloride, the first six strong lines were observed up to 8 GPa. The number of lines recorded were 6 and 5 for silicon and magnesium oxide, respectively. For zircon, the first 10—12 strong lines were observed up to 8 GPa, in contrast to 4—6 lines observed in an earlier study.[32] However, if one is dealing with samples containing elements of high atomic numbers, and also of high crystal symmetry so that the diffracted intensity is large and the number of lines are not many, it may be possible to mix the epoxy to a mixture of the sample and the standard without facing serious problems of overlap or low intensity.

The use of epoxy as a pressure-transmitting medium helps only to reduce (and not eliminate altogether) the uniaxial stress component and its effect on the measured lattice parameters, possibly down to a limit which is below the present limits of detection. This leads to a marked improvement over the conventional method of mixing the sample and the standard in the case of samples which are capable of supporting large uniaxial stress components.

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